SUBSTANCES WITHOUT CHEMISTRY

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SUBSTANCES without chemistry must necessarily be elements, for, if substances form compounds with other substances, they thereby come into the realm of chemistry. The group of elements to be considered are found in the atmosphere, but their presence was not suspected until less than twenty years ago, when within a comparatively short space of time, helium, neon, argon, krypton and xenon were discovered. Of these, xenon is present only to the extent of one part in 170,000,000 of air, but argon constitutes nearly one per cent. of the atmosphere. Yet, with the exception of the chemist Cavendish, no one seems to have suspected its presence and Cavendish merely suggests the existence of some unknown gas.

In this paper there will be several digressions that may seem foreign to the subject in hand, but that are intended to help in elucidating the main topic or to explain words or phrases necessarily employed.

Two classes of elements have eluded for a longer or shorter time the researches of chemists. One class is represented by fluorine. The story is told of a man who claimed to have discovered a universal solvent and, when asked to exhibit it, replied "How can I? It is impossible to get any dish to contain it." Fluorine is somewhat of this nature. The existence of the element was suspected. The mineral fluorspar was known to contain calcium, which is the metallic part of limestone, and was suspected of containing another element similar to chlorine, which is the non-metallic part of common salt. But this element could not be got from fluorspar in a manner analogous to that by which chlorine was obtained from common salt. The element could be detached from the calcium, but only to combine with something else. When common salt is acted on with concentrated sulphuric acid (the oil of vitriol of the newspaper reporter) hydrochloric acid, a very irritating gas, is produced, and this gas with suitable chemicals gives chlorine. When fluorspar is acted on with concentrated sulphuric acid a still more irritating gas, hydrofluoric acid, is produced. Its solution in water produces, on the flesh, very distressing sores exceedingly difficult to heal. Both the gas and its solution act on glass and the etching of glass is frequently done by the use of hydrofluoric acid. But hydrofluoric acid could not be made to act on any chemical in such a way as to set free fluorine. The element entered into innumerable combinations, but did not appear alone. Thus, though chemists had consid-

ered that there must be the element and had formed a pretty fair idea of what its appearance and properties would be, still, this element, that Davy in 1813 stated to exist in fluorspar, was not isolated till, in 1886, Moissan by the use of the electric current at a low temperature, with specially resistant apparatus, obtained the element in the form of a gas whose properties were almost identical with those predicted.

Another class of elements are elusive because their presence is not suspected, and their properties are somewhat similar to those of known elements. The metal cæsium belongs to this class. In 1846, Plattner analyzed the mineral *pollux,* but could not get the constituents as found by his analysis to add up to one hundred per cent. He published his figures, however. In 1860 Bunsen and Kirchhoff discovered the element cæsium, and it turned out that Plattner's analysis needed only the correction that the mineral pollux contained cæsium, instead of what he thought was potassium. The properties of potassium and cæsium are very similar; potassium is a common metal, while cæsium is not, and it was not till the delicate methods of the spectroscope were devised that any ready means of distinguishing between the two elements was available. The five elements discovered in the air are sufficiently similar to nitrogen as not to be distinguished from it until chemists had their attention turned to the matter by experiments undertaken with an entirely different object in view.

In 1785 the Honorable Henry Cavendish, of whom the Frenchman Biot in his obituary notice remarked that he was "the richest of all scientists, and the most scientific of all the rich," made some experiments with air by passing electric sparks through it, in this way producing nitric acid and potassium nitrate (saltpeter). It is notable that this process that Cavendish first applied on the small scale and with excessive toil is now carried out on the commercial scale in Norway and Sweden, where electric power is cheap. Up till three or four years ago, however, not more than one per cent. of the world's supply of nitric acid was made in this way, since, for the most part, it was cheaper to get it from sodium nitrate or Chili saltpeter, so named from its place of origin in South America. But as 50–80 per cent. of all the more important explosives consist of nitric acid and as Germany must be pretty well shut off from South America, she must either have laid in an enormous stock of nitric acid before the war or the electric process must have since been greatly developed, unless, indeed, she has gone back to the primitive method by which saltpeter is made in the villages of India, which is very unlikely.

When Cavendish passed electric sparks through air and oxygen added as required, he found that though the volume of air diminished until it became very small, it was impossible for him to reduce it to zero; a little gas remained. He had recognized the air as containing

the gases which we now call oxygen and nitrogen, and he said that if what remained behind was not nitrogen its volume was not more than one one hundred and twentieth that of the nitrogen. He did not carry his experiments any farther, a course of action not to be wondered at when we learn that he and his assistant in carrying the investigation to this point had already kept turning the handle of the frictional electric machine for the not inconsiderable period of three weeks. Most people would count that a long enough time to keep the nose to the grindstone.

It is now possible by simply switching on an electric current to obtain the same result in a much shorter time; but, although for the last fifty years or more Cavendish's experiment could have been repeated with ease, no one thought of attempting it; and text-books in chemistry continued calmly to assert that air consists on the average of 20.96 per cent. of oxygen and 79.04 per cent. of nitrogen.

Attention was drawn to the subject owing to an investigation carried on by Lord Rayleigh, with no thought of the wonderful outcome of his work, which was started for an entirely different purpose. He set out to determine the densities of various gases, in the first place the relative densities of oxygen and hydrogen, at which he worked from time to time during ten years 1882–1892. After that he determined the density of oxygen and nitrogen and of air with a view to determining the percentage of the two gases in the atmosphere. Lord Rayleigh prepared the gases in different ways. Oxygen was prepared in three different ways, but, no matter in what way it was prepared, its density was always the same. Such was not the case with nitrogen, however. Of the nitrogen obtained from five different chemical compounds which Lord Rayleigh employed, the amount contained in the globe that he used weighed on the average 2.29900 grams, while the nitrogen obtained in three ways from the air weighed on the average 2.31049 grams. Translated into English measures, this means that approximately three pints of nitrogen got from air weighed about one seventh of a grain more than the same volume of nitrogen from the chemical compounds.

The ratio between the two weights was not far different from that between an ordinary letter, before and after the stamp is put upon it; but the actual difference in weight was only about one tenth the weight of a postage stamp. But the greatest difference in the weight of the nitrogen obtained from the different chemical compounds was not more than one seventieth the weight of a stamp, while in most of the experiments the difference was much less. It was evident then that the difference noticed between atmospheric nitrogen and what might be called chemical nitrogen could not be due to Rayleigh's errors in weighing.

Rayleigh at first inclined to the opinion that atmospheric nitrogen

was the real nitrogen and that chemical nitrogen was lighter because of the presence of some lighter substance mixed with it, but this opinion was proved to be incorrect. Then it was suggested that possibly atmospheric nitrogen was heavier, because some of the molecules contained more atoms than real nitrogen. There is pretty good proof that the molecules of nitrogen consist of two atoms; the suggestion was that atmospheric nitrogen might contain a certain percentage of molecules consisting of three or four atoms. It has been long known that electric discharges through oxygen produce an effect of this kind. Part of the oxygen is converted into ozone, which is denser, so that the same volume would have greater weight. It was proved, however, that no similar phenomenon occurs with nitrogen.

At this stage Professor Ramsay joined forces with Lord Rayleigh and, by passing nitrogen obtained from air through a red-hot tube containing magnesium, he found that, though most of the gas combined with the magnesium, a small portion did not do so, though the process was continued for ten days. This small portion was about one eighty-fourth of the whole. When chemical nitrogen was subjected to the same treatment it was entirely absorbed.

Lord Rayleigh repeated under more favorable conditions and with larger quantities of air, Cavendish's experiment of passing sparks through a mixture of air and oxygen and got a gas identical with that obtained by Ramsay. This gas is heavier than nitrogen in the ratio of ten to seven. Many experiments have been tried, but without success, to make it combine with other substances. It is inert, hence the name argon from the Greek word with that meaning. It has no chemistry—all the experiments possible with it are physical. Its inertness kept it a long time undetected. Its inertness makes it of no chemical value now that it has been found, except in so far as its inertness may affect chemical theory. Ramsay, having found argon in the air looked about for some other source. While doing so he received a letter from Miers, the mineralogist, at that time connected with the British Museum, who suggested that it might be well to examine some uraninites (varieties of pitchblende largely uranium oxide). Hillebrand, one of America's most noted analysts, had obtained a gas from uraninite which he supposed to be nitrogen. Ramsay thought it improbable that Hillebrand's methods would prepare nitrogen from any of its compounds and he reexamined one of the minerals used by Hillebrand, namely, clèvite. He did *not* find argon, but he found a gas not previously discovered on the earth, though it had been found in the luminous atmosphere of the sun, by means of the spectroscope in 1868, or about twenty-six years previously.

It may be noted that the name *helium* had been given to this element not *helion*. Nearly all the metals except the very common ones

that have been known for centuries terminate in *-um* or *-ium,* for instance, platinum, aluminium, sodium, potassium. On the other hand, several of the non-metals terminate in *-on,* for example, carbon, boron, silicon and all of the elements except helium that are similar to argon. When helium was discovered in the sun, from which it got its name, there was nothing to show that it was not a metal, and, though the Green termination *-on* would have been more suitable, it is not likely to be adopted. At the present time, the spectroscope reveals in some nebulæ, an element not found on the earth as yet, and to it the name *nebulium* is given.

Hillebrand was unfortunate in not discovering helium. The gas that he obtained responded to the tests for nitrogen, though not so rapidly as he had reason to expect with pure nitrogen. He and his assistant jokingly suggested that they might have found a new element, but as they thought it unlikely they did not pursue the investigation and so helium remained undetected for five years longer. Ramsay showed that the gas from clèveite contained 12 per cent. of nitrogen. This Hillebrand detected, but not the far larger amount of helium.

Hillebrand is not the only chemist to make a similar error. A bottle containing a heavy reddish-brown liquid was sent to Liebig for analysis. He thought that it was chloride of iodine and did not investigate it very thoroughly. Some time afterwards, in 1826, Balard discovered bromine, and Liebig realized then that his specimen was bromine, and he gave it a place in his special cabinet for storing mistakes. He was accustomed to cite it as an example of how one may miss a great discovery.

Helium is found in a number of minerals, usually in cavities of microscopic size and under a pressure of several atmospheres. In several places in Kansas, natural gas has been obtained containing more than one per cent. of helium, while in a number of other localities natural gas contains a less proportion. It is also found in some mineral waters. Experiments, carried out by Rayleigh and Ramsay, seemed to indicate that helium does not exist in the air, and Dr. Johnston Stoney gave a mathematical proof that it could not permanently remain in the air, as it is so light that the earth's attraction would not be sufficient to retain it. Whether it is produced rapidly enough to keep up the supply or that there is some unknown factor not taken into account by Stoney, the fact is that helium has been found in the atmosphere to the extent of about one volume in 185,000. Helium is only about one seventh as heavy as air and so the proportion by weight is correspondingly less. It may be added that hydrogen is even lighter than helium and even hydrogen is found to the extent of one part or more in 100,000.

The liquefaction of helium is of interest, but before taking it up it will be well to sketch the history of the liquefaction of gases. In 1823 Faraday liquefied chlorine. Other gases were liquefied by him in the

same manner. But some gases resisted liquefaction by this means, conspicuously those existing in the atmosphere. These were called permanent gases. But in 1877, Pictet and Cailletet independently succeeded in obtaining a few drops of liquid air. In 1895, processes were invented by which air could be liquefied by the gallon. Hydrogen resisted liquefaction, till Dewar, in 1898, succeeded in reducing it also to the liquid form. There was left one gas only, namely helium, unliquefied. A sufficiently low temperature was not available. But in 1908 Omnes gained the distinction of liquefying this last remaining gas and obtained a liquid that boils at 4.5 Centigrade degrees above the absolute zero of temperature, but that, so far, has not been solidified, though a temperature as low as 2.5° absolute has been reached.

A word of explanation should perhaps be given as to what is meant by absolute temperature. The difference between our coldest winter weather and hottest summer is a little more than half the difference between freezing and boiling water, which on the Centigrade thermometer is one hundred degrees. The melting point of ice is zero on the Centigrade scale, the boiling point of water is 100° C. Bright red heat is about 1,000°; furnaces for iron is 1,300–1,700°; the melting point of tungsten is 3,000°; in the electric furnace a temperature of 3,500° C. has been reached, perhaps even a higher temperature. Probably no temperature higher than 4,000° C. has been made by man, but the temperature of the sun has been estimated at 6,000° C. There is nothing to prevent us conceiving of a temperature of 10,000° or even of 100,000° in the same sense as we can conceive one hundred million dollars. While, however, we have no difficulty in attaining a temperature of seven or eight hundred degrees and can attain a much higher temperature, we not only have not reached a temperature of three hundred degrees below zero, but we are almost certain that such a temperature is impossible. Several lines of argument lead to the conclusion that at —273° C. a body would be absolutely without heat and that any lower temperature is therefore impossible. So —273° C. is called the absolute zero and helium has been cooled to —270.5° C. or 2.5° absolute without having been frozen. The difference in temperature of a room very slightly chilly and almost comfortably warm is about 2.5°.

Liquid helium is about one seventh as dense as water, which is approximately the same ratio as the gas bears to air at the ordinary temperature. When boiling the volume of gaseous helium is only eleven times that of the liquid, while steam is nearly seventeen hundred times the volume of the water from which it is produced.

In 1898, Ramsay and Travers published accounts of three other gases found in the air, *krypton* and *xenon* being heavier than argon and *neon* being lighter. The two heavier ones were got from liquid air. Liquid air is produced on the commercial scale; one of its chief uses is

as a source of oxygen. Liquid air consists mainly, of course, of nitrogen and oxygen and when it boils nitrogen volatilizes more readily than oxygen, just as alcohol distils off from water with which it is mixed. So oxygen is left behind just as water is left behind, a somewhat bluish liquid with the peculiar property of being magnetic. After the nitrogen, the oxygen volatilizes and when it has nearly gone the small quantity of liquid left is mainly argon but there is a little krypton and xenon. Ramsay and Travers used about six gallons of liquid air, Moore some time afterwards made use of the residue of a quantity of liquid air which will by most people be considered really large, namely, one hundred and twenty tons. There is one part of krypton in twenty million parts of air by volume and one part of xenon in one hundred and seventy million parts of air. Thus 120 tons of air would yield between twenty-five and thirty cubic inches of xenon and about eight times as large a volume of krypton. The latter name refers to the gas being hidden by or in the large quantity of argon which it closely resembles. There is a rare metal *lanthanum* whose name has a similar origin, since the properties of its compounds are so similar to those of another metal that it escaped notice for a considerable length of time.

The *aurora borealis* has been the object of admiration and speculation for centuries. Cavendish, whose connection with the main subject of this paper was so conspicuous, calculated the height of the aurora to be from fifty-two to seventy-one miles and probably this calculation is not far wrong. One of the theories regarding the cause of the aurora is that it is due to electrical discharge through the rarefied atmosphere and De la Rive of Geneva made a model to represent the discharge influenced by a magnet in much the same way as terrestrial magnetism affects the aurora.

When the aurora was examined by the spectroscope a very intense green line, not known to belong to any element, was found. When Ramsay was working with krypton, his assistant, Baly, examined its spectrum and noticed among a number of other lines a brilliant green one whose wave-length he measured carefully. No sooner were his results published than letters were sent to Ramsay and to the scientific press pointing out that this wave-length corresponded to that of the most important line in the spectrum of the aurora.

Neon does not call for special comment. It is lighter than air and has a spectrum not already known, perhaps receiving its name of *new* from this fact. There is one part in about 55,000 of air.

All these elements are incapable of forming compounds; they are all inert; they have no chemistry. The atomic weight of most elements is arrived at from chemical considerations, the analyses of compounds, and such like experiments. The atomic weight of these elements can not be arrived at in this way. The density as compared with hydrogen can be determined, but this alone will not fix the atomic weight, the relative

weight of the atom compared with the atom of hydrogen. One of the most important means for arriving at the number of atoms in the molecule, and in that way the atomic weight, is by determining the velocity of sound in the gas. This velocity is found in a very ingenious manner in a quantity of gas contained in a glass tube a few feet long and a small fraction of an inch in diameter. The determination of the atomic weight of an element is one of the most important investigations connected with it and for these elements physical not chemical means must be used.

Belonging to the same group of elements is still another gas, *niton,* which is not found in measurable quantity in the air. It is given off by the element radium and is sometimes called radium emanation. That it is not found in the air is not to be wondered at, since if a quantity equal to that of argon in the atmosphere were suddenly introduced into the air, it would within three months diminish to less than the quantity of xenon changing from one part in a hundred to one part in two hundred million of air. This is because niton decomposes so rapidly. In less than four days any quantity will diminish to one half what it was at the beginning of the time. One of the products of decomposition is helium, another is a substance metallic in character which itself readily disintegrates. This substance deposits on a negatively charged body brought into contact with niton, and the fact that a negative wire in the atmosphere acquires such a deposit, which may be rubbed off or dissolved by ammonia, is taken as indication of the presence in the air of an infinitesimal quantity of niton. Any further discussion of this matter would lead too far afield.

The above are all the elements *known* to belong to this group; but the Russian chemist Mendelèef, whose arrangement of the elements according to their atomic weights in series and in groups was epoch-making in the science of chemistry, suggests that there may be two other elements in the group, elements very much lighter than hydrogen, one of them almost infinitely lighter. One is the corona of the sun, the other the luminiferous ether. At present we have no means of testing Mendelèef's hypothesis.